

TREATMENT OF POME via CHITOSAN BASED FLOCCULATION:
STUDY THE EFFECT OF DOSAGE CHITOSAN IN REMOVAL OIL FROM POME

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I declare that thesis entitled “Treatment of POME via Chitosan based flocculation: Study the effect of dosage chitosan in removal oil from POME” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

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Date : 9 May 2008

To my beloved mother, family, friend and people around me

*“Forgive us when we fall down and lift us back up and rebuild our walls, so that
the enemy is defeated in our lives”*

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ABSTRACT

The treatments of palm oil mill effluent (POME) have been a topic of research in Malaysia. These effluents need to be properly treated before it is released to watercourse and minimize the environmental hazard. This research is conducted to evaluate the treatment of palm oil mill effluent (POME) using chitosan based flocculation. Chitosan is a biological product which was believed it is useful in water treatment as adsorbent to remove oil from wastewater. A study was conducted in the laboratory to compare chitosan concentration in different volume of dosage. The sample were undergo flocculation process by using Jar Test where six beaker of sample was treated with varies volume dosage. The comparison was made by analyzing their oil removal efficiency, reduction of suspended solid, turbidity, BOD and COD and as well as pH adjustment. The result indicated that chitosan concentration at ratio of 1wt% chitosan in 1% was performed better in increasing of volume doses and 2%wt chitosan in 7% acetic acid was better at optimum dosage more than 12ml. In conclusion, it shows that chitosan was effective in removal oil from POME with more than 90% efficiency.

ABSTRAK

Pemulihan hampasan minyak sawit telah menjadi satu isu kajian di Malaysia. Hampasan-hampasan ini harus dirawat sebelum ianya disalurkan ke sumber air disamping mengurangkan pencemaran alam sekitar. Kajian ini dibuat untuk menganalisa pemulihan hampasan minyak sawit menggunakan chitosan melalui proses pemendapan. Chitosan merupakan produk biologi yang dipercayai ianya boleh digunakan di dalam pemulihan air sebagai penyerap yang boleh memisahkan minyak daripada kumbahan. Satu kajian telah dijalankan di makmal untuk membanding kandungan chitosan dalam isipadu dos yang berbeza. Sampel akan melalui proses pemendapan dengan menggunakan Jar Test iaitu enam bikar yang berisi sampel dirawat dengan dos isipadu yang berbeza. Perbandingan akan dibuat dengan menganalisa perkadaran minyak yang dipisahkan, pengurangan pepejal atau bahan yang terbuang, kekeruhan, BOD dan COD dan nilai pH. Keputusan menunjukkan kandungan chitosan pada nisbah 1% chitosan dalam 1% asid asetik memberikan hasil yang terbaik apabila isipadu dos meningkat dan 2% chitosan dalam 7% asid asetik pada optimum dos lebih daripada 12ml. Ini membuktikan bahawa chitosan sememangnya berkesan dalam memisahkan minyak daripada hampasan minyak sawit dengan lebih 90% perkadaran.

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LIST OF SYMBOLS

POME	= Palm Oil Mill Effluent
BOD	= Biological Oxygen Demand
COD	= Chemical Oxygen Demand
rpm	= Rotation per minute
NTU	= Nephelometric Turbidity Units
DO	= Dissolved Oxygen
D₁	= initial DO of the diluted wastewater sample about 15 min after preparation
D₂	= final DO of the diluted wastewater sample after incubation for 5 days
ppm	= Part per million
CPO	= Crude Palm Oil
mg/L	= milligram/Liter

CHAPTER 1

INTRODUCTION

1.1 Background

Wastewater treatment capability is one of the most important components in the palm oil production. This capability is normally used to treat a large volume of POME generated during the production of CPO before the effluent is safely discharged to the surrounding environment through water canal or river. Every year and nowadays there has been an increasing concern for environmental risk of industrial activities associated with extraction, hydrocarbons, food processing, and transportation. This activity has given the effect to the natural environment and creates a major ecological problem throughout the world. The concentration of oil in effluents from different industrial sources is found to be as high as 40,000mg/l (Guo and Lua, 2000). Most of industrial wastewater can lead to severe problems in different treatment stages. Oil in wastewaters has to be removed in order to prevent interfaces in water treatment units, reduce fouling in process equipment, avoid problems in biological treatment stages and comply with water discharge requirements.

Current methods for such wastewater treatment include coagulation/flotation, sedimentation, flotation, filtration, membrane process and biological process. Among the current methods flocculation process is one of the effective methods that used in wastewater systems. Flocculation of waste oil using flocculants agent such as chitosan is highly selected to be used in this research because it is low cost material and the resources is easy to find.

Chitosan is believed as best adsorbent for oil removal from wastewater (Tseng *et al.*, 2001). This material is only commercially extracted from crustaceans (shrimp, crab, krill) primarily because a large amount of the crustacean's exoskeleton is available as a by product of food processing. Chitosan is a natural carbohydrate biopolymer derived from deacetylation (DA) of chitin, a major component of the shells of crustacean such as crab, shrimp, and crawfish, after cellulose (No and Meyers, 1989; Ruiz-Herrera, 1978). Chitosan has been used in a variety of practical fields including wastewater management, pharmacology, biochemistry and biomedical. (Majeti, 2000; Feng *et al.*, 2000).

The main use was still as a non-toxic flocculent in the treatment of organically polluted wastewaters. It also increases the absorption capacity of chitosan compared to that of chitin, which only have a small percentage of amino groups. (Evans *et al.*, 2002; Wu *et al.*, 2001; Lu *et al.*, 2001). Besides removing metal ions, recent research study has revealed that chitosan also has the ability to remove oil in POME with 99% reduction capability. (Ahmad *et al.*, 2005).

1.2 Problem Statement

Over the last few decades, the Malaysian palm oil industry has grown to become an important agriculture-based industry. With increased cultivation and production of palm oil in the region, the disposal of the processing waste is becoming a major problem that must be appropriately addressed. There a lot of scientists make a research on this pollutant where researches including how to treat the oil waste and then how to produce it become more usefully to human. For example palm oil wastewater can be purified to produce drinking water. The major problem in waste water field is the needing of high cost of the purification installations and the necessity of utilizing the waste product. For the reason, the use of low cost materials as sorbent for oil removal from wastewater has been highlighted. One of the exploitation is the use of natural wastes because of the low cost, high availability of these materials and no need for complicated regeneration process. Chitosan is believed to be the best natural adsorbent to remove oil from wastewater (Tseng *et al.*, 2001). This adsorbent is only commercially extracted from crustaceans like shrimp, crab, and krill. Removal of oil from other industrial wastewater sources by using chitosan has not been extensively studied by many scientists, especially in the oil and gas industry. The environment and properties of such wastewater differs in many ways than the palm oil industry. Flocculation of residue oil and suspended solid from palm oil mill effluent (POME) an oily effluent using a biodegradable biopolymer, chitosan was explored in this study using a flocculator.

1.3 Objective of the study

The main objectives of this research are to study the effect of different dosage of chitosan in removal oil based flocculation.

1.4 Scope of research work

In order to achieve the objective, several scopes of work have been identified:

1. To study the effect of chitosan concentration in different volume of dosage in order to remove oil from oily industrial wastewater.
2. To evaluate the oil removal efficiency.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The research of new way involving the removal of oil waste from wastewater by using flocculation treatment based on oil waste nature. The process of flocculation use to create a sizeable flake. One must add another chemical called flocculent in order to facilitate the formation of flakes. The flocculent that was using in the research is chitosan which is a natural products and the resource is easy to find because it is low cost material. Chitosan can be used in water processing engineering as a part of a filtration process. The wastewater that was going to be treat for this research project is Palm Oil Mills Effluent (POME) which our country lately have been focusing on palm oil industry.

2.2 Chitosan

Chitosan is a linear polysaccharide composed of randomly distributed β -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Chitosan has been widely used in vastly diverse fields, ranging from waste management to food processing, medicine and biotechnology (Savant and Torres, 1995). Chitosan is produced commercially by deacetylation of chitin. From wikipedia, the degree of deacetylation (%DA) can be determined by NMR spectroscopy, and the %DA in commercial chitosan is in the range 60-100%. Chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependent on pH and the %DA value.

Chitosan is an important additive in the filtration process. Sand filtration apparently can remove up to 50% of the turbidity alone while the chitosan with sand filtration removes up to 99% turbidity (Alan, 2002). Chitosan is used mostly applied textile, printing, leather, cigarette, plastics, foodstuff, fodder, color film, medicine and paper-manufacturing industry, biological-engineering industry, agriculture-protecting industry, dirty water-cleaning industry, etc.

2.3 Palm Oil

Oil palm is an important crop in Malaysia. Approximately 11.9 million tones of crude palm oil (CPO) were produced that amounted to RM 14.79 billion in the year 2002(Edoardo *et al.*, 2002). The process to extract the oil requires significantly large quantities of water for steam sterilizing the palm fruit bunches and clarifying the extracted oil. It is estimated that for one tone of crude palm oil produced, 5-7.5 tones of water are required, and more than 50% of the water will end up as palm oil mill effluent (POME). Thus, while enjoying a most profitable commodity, the adverse environmental impact from the palm oil industry cannot be ignored. Based on the current annual rate of oil palm harvesting, some 4.5 million metric tones of effluents are being produced and discharged into the rivers.

POME is a colloidal suspension of 95-96% water, 0.6-0.7% oil and 4-5% total solids including 24% suspended solids originating from the mixture of a sterilizer condensate, separator sludge and hydro cyclone wastewater . The raw or partially treated POME has an extremely high content of degradable organic matter, which is due in part to the presence of unrecovered palm oil. POME characteristic and standard discharge limit is illustrated in Table 2.1. In order to regulate the discharge of effluent from the crude palm oil industry as well as to exercise other environmental controls, the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Order, 1977, and the Environment Quality (Prescribed Premises) (Crude Palm Oil) Regulations, 1977, were promulgated under the Environmental Quality Act, 1974. Due to these factors, the palm oil industry faces the challenge of balancing the environmental protection, its economic viability and sustainable development. There is an urgent need to find a way to preserve the environment while keeping the economy growing (Abdul Latif *et al.*, 2003). This highly polluting wastewater can therefore cause severe pollution of waterways due to oxygen depletion and other related effects. The presence of oil-waste makes the bio-degrading process of the

effluents difficult as oil inherently difficult to disintegrate; hence this will lead to ruin the natural river or lake ecosystem (Edoardo *et al.*, 2002).

PARAMETERS	STANDART LIMIT mg/L	CONCENTRATION mg/L
pH	5-9	4.7
Oil and grease	50	4000
BOD	100	25000
COD	-	50000
Total Solids	-	40500
Suspended solids	400	18000
Total nitrogen	150	750

Table 2.1: Characteristics of POME and its respective standard discharge limit by the Malaysian Department of the Environment. (Abdul Latif *et al.*, 2003)

2.4 Flocculation

Flocculation is a gentle mixing stage, increases the particle size from submicroscopic microfloc to visible suspended particles. The microflocs are brought into contact with each other through the process of slow mixing. Collisions of the microfloc particles cause them to bond to produce larger, visible flocs called pinflocs. The floc size continues to build through additional collisions and interaction with inorganic polymers formed by the coagulant or with organic polymers added. Macroflocs are formed. High molecular weight polymers, called coagulant aids, may be added during this step to help bridge, bind, and strengthen the floc, add weight,

and increase settling rate. Once the floc has reached its optimum size and strength, the water is ready for the sedimentation process.

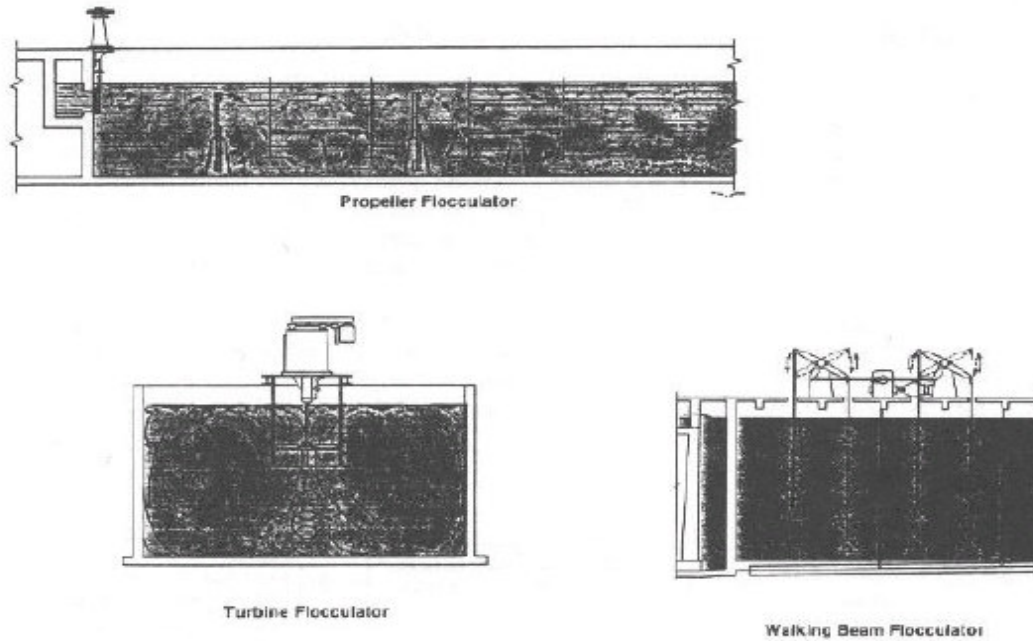
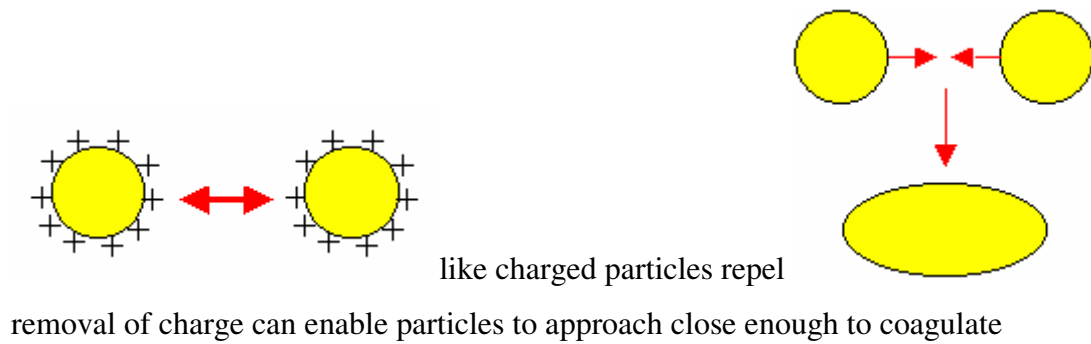


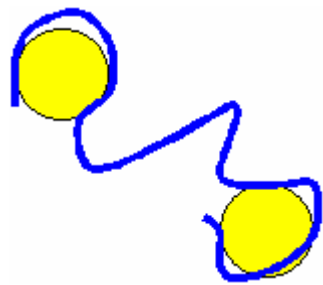
Figure 2.1 Design contact times for flocculation range from 15 or 20 minutes to an hour or more.

2.4.1 Flocculation Mechanisms

Charge Neutralisation:



Bridging Flocculation:



Polymer chains can “bridge” particles to create larger masses that settle out

Flocculants are important in water treatment for mining wastes, sewage treatment as well as many other similar processes. Flocculants are charged polymers used in industry for clarifying suspensions. They cause suspended colloidal matter to aggregate, forming particles that are large enough to settle out under gravity. Both

cationic polymers (containing positive charges) and anionic polymers (containing negative charges) are used for different applications. A typical anionic flocculant is a copolymer of acrylamide and acrylic acid, made by inverse emulsion polymerization. The essential mechanisms by which flocculants work are charge neutralisation and bridging. Charge neutralisation allows particles to get closer to each other by reducing the electrostatic interactions between them (when they can approach more closely, they can join together coagulate). Bridging flocculation involves polymer chains sticking to multiple particles, making an aggregate large enough to settle out.

2.4.2 Chitosan as Flocculants

Chitosan is a natural polysaccharide comprising copolymers of glucosamine and *N*-acetylglucosamine, and can be obtained by the partial deacetylation of chitin, from crustacean shells, the second most abundant natural polymer after cellulose (Illum, 1998; Nunthanid, J. and Puttipipatkachorn, 2001). Chitosan has been commonly used in vastly diverse fields, ranging from waste management to food processing, medicine and biotechnology (Savant and Torres, 1995). It becomes an interesting material in pharmaceutical applications (Illum, 1998) due to its biodegradability and biocompatibility (Borchard and Junginger H.E, 2001), and low toxicity (Karlsen and Skaugrud, 1991). Chitosan has found wide applicability in conventional pharmaceutical devices as a potential formulation excipient (Singla and Chawla, 2001). The use of chitosan in novel drug delivery as mucoadhesive (Lehr *et al.*, 1992), peptide (Bernkop-Schnurch and Kast, 2001) and gene delivery (Borchard, 2001), as well as oral enhancer (Thanou *et al.*, 2001). Since chitosan is a new substance, it is important to carry out precise standardization for its pharmaceutical and biomedical applications like other auxiliary substances (Knapczyk *et al.*, 1989).